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(54) **IN SITU NUCLEATION FOR NANOCRYSTALLINE DIAMOND FILM DEPOSITION**

(71) Applicant: **Applied Materials, Inc.**, Santa Clara, CA (US)

(72) Inventors: **Sze Chieh Tan**, Singapore (SG); **Vicknesh Sahmuganathan**, Singapore (SG); **Eswaranand Venkatasubramanian**, Santa Clara, CA (US); **Abhijit Basu Mallick**, Sunnyvale, CA (US); **John Sudijono**, Singapore (SG)

(73) Assignee: **Applied Materials, Inc.**, Santa Clara, CA (US)

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C23C 16/455	(2006.01)
B82Y 40/00	(2011.01)

(52) **U.S. Cl.**

CPC ***C23C 16/279*** (2013.01); ***C23C 16/0227*** (2013.01); ***C23C 16/45536*** (2013.01); *B82Y 40/00* (2013.01)

(58) **Field of Classification Search**

None

See application file for complete search history.

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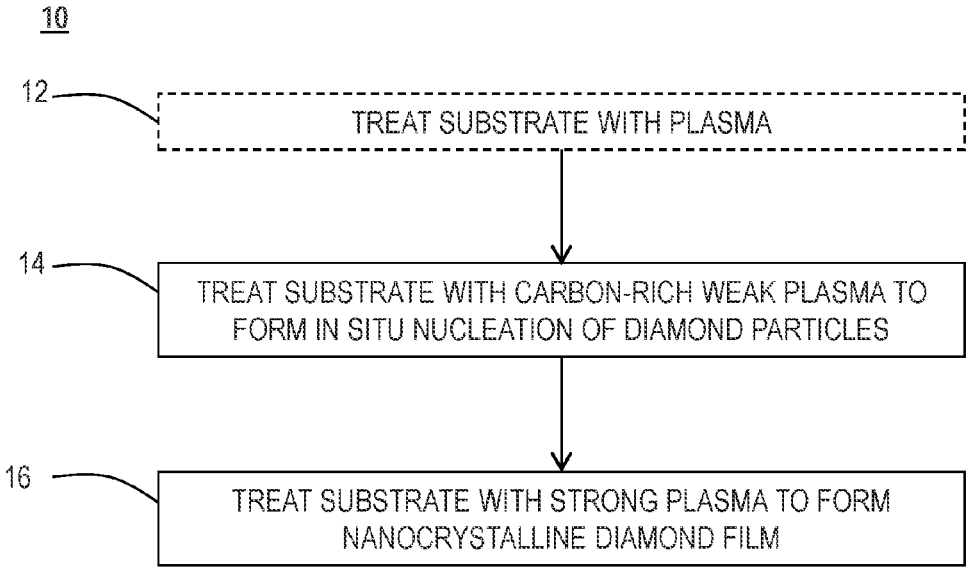
Primary Examiner — Jose I Hernandez-Kenney

(74) *Attorney, Agent, or Firm* — Servilla Whitney LLC

(57) **ABSTRACT**

Methods of depositing a nanocrystalline diamond film are described. The method may be used in the manufacture of integrated circuits. Methods include treating a substrate with a mild plasma to form a treated substrate surface, incubating the treated substrate with a carbon-rich weak plasma to nucleate diamond particles on the treated substrate surface, followed by treating the substrate with a strong plasma to form a nanocrystalline diamond film.

14 Claims, 2 Drawing Sheets



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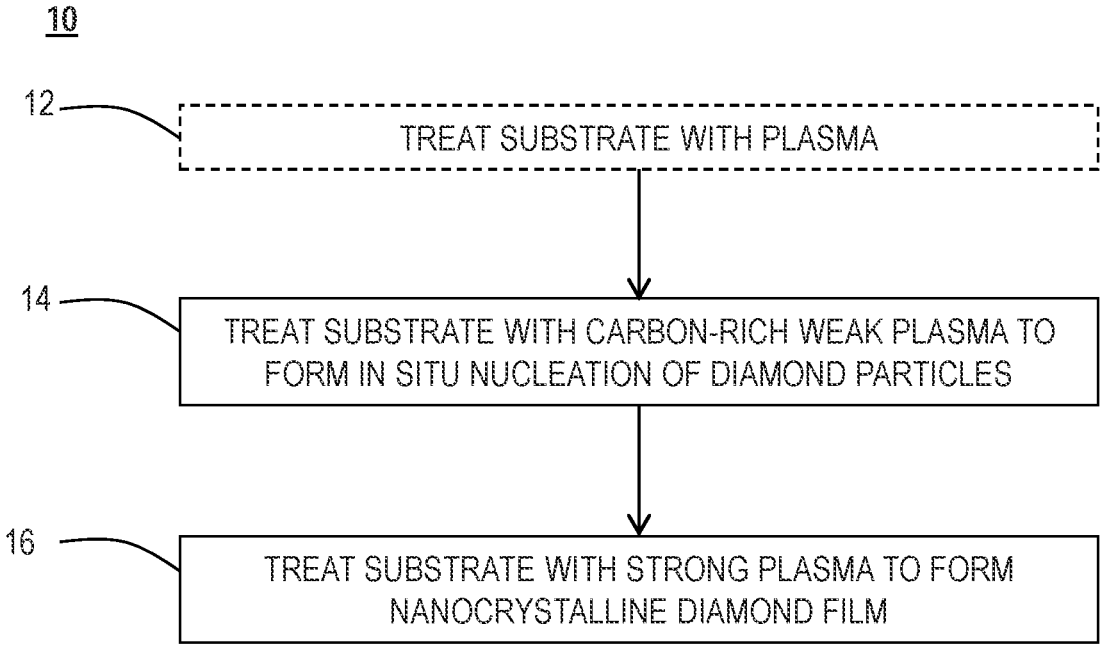
10
12
TREAT SUBSTRATE WITH PLASMA
14
TREAT SUBSTRATE WITH CARBON-RICH WEAK PLASMA TO FORM IN SITU NUCLEATION OF DIAMOND PARTICLES
16
TREAT SUBSTRATE WITH STRONG PLASMA TO FORM NANOCRYSTALLINE DIAMOND FILM

FIG. 1

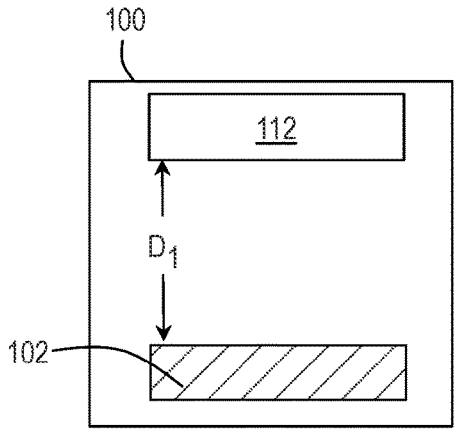

FIG. 2A

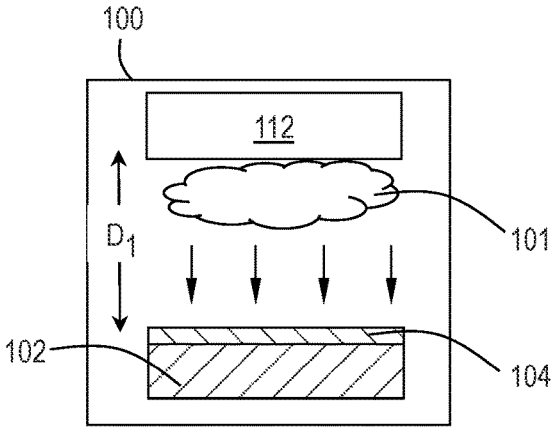

FIG. 2B

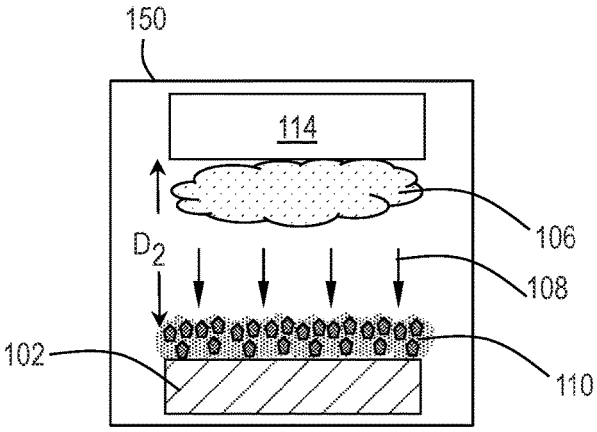

FIG. 2C

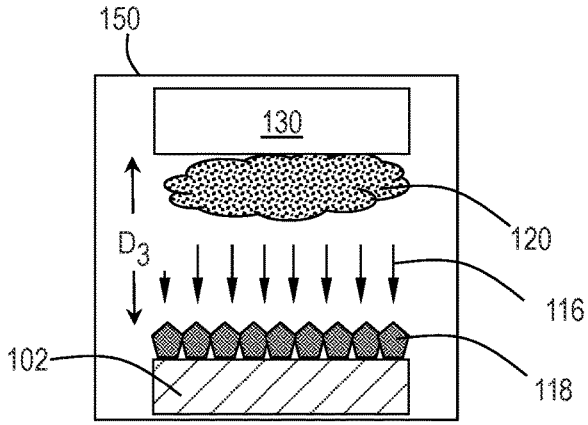

FIG. 2D

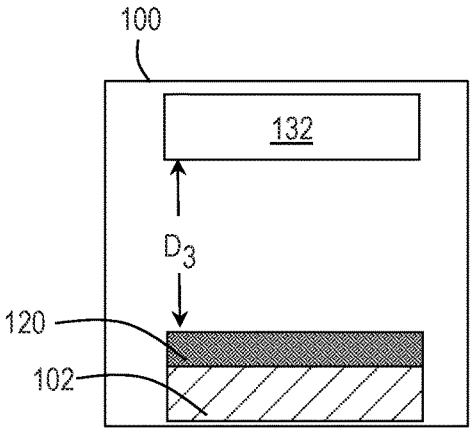

FIG. 2E

IN SITU NUCLEATION FOR NANOCRYSTALLINE DIAMOND FILM DEPOSITION

TECHNICAL FIELD

Embodiments of the present disclosure pertain to the field of electronic device manufacturing, and, in particular, to integrated circuit (IC) manufacturing. More particularly, embodiments of the disclosure provide methods of depositing diamond-like carbon hard mask films, which can be used for patterning applications.

BACKGROUND

As the semiconductor industry introduces new generations of integrated circuits (ICs) having higher performance and greater functionality, the density of the elements that form those ICs is increased, while the dimensions, size, and spacing between the individual components or elements are reduced. While in the past, such reductions were limited only by the ability to define the structures using photolithography, device geometries having dimensions measured in μm or nm have created new limiting factors such as the conductivity of the metallic elements, the dielectric constant of the insulating material(s) used between the elements, or challenges in 3D-NAND or DRAM processes. These limitations may be addressed by more durable and higher hardness hard masks.

Diamond is a material with high hardness, chemical inertness, high thermal conductivity, and good optical transparency, making it promising in microelectronic applications. Diamond has emerged as a promising candidate for a myriad of microelectronic applications. The large discrepancy in the surface energies of diamond and silicon (6 J cm^{-2} vs. 1.5 J cm^{-2}), low sticking coefficients of the gaseous precursors (e.g., hydrocarbon radicals) and strong competition from the nondiamond phases, however, typically result in poor diamond nucleation density (~10^4 cm^{-2}) on untreated silicon.

To address poor diamond nucleation density, the substrate is usually pre-treated (e.g., mechanical abrasion or microchipping) and/or seeded with nano-diamond (ND) particles prior to deposition. Such seeding methods, however, consist of multiple solution-based procedures which are cumbersome and not cleanroom compatible. Bias-enhanced nucleation (BEN), on the other hand, is one of the few nucleation techniques that can be performed in-situ. It involves the bombardment of methane-rich (4-10%) ionized gas species on the surface of a negatively-charged biased substrate, allowing the formation of a carbide layer with improved substrate adhesion. With BEN, nucleation densities greater than 10^{11} cm^{-2} had been reported. Unfortunately, the application of BEN is limited by the presence of substrate surface damages (e.g., in the form of holes as deep as 2-3 μm in diameter), difficulty in applying bias uniformly over large areas, and the need for a conductive substrate.

Hence, from a large-scale manufacturing and production perspective, both solution-based seeding of NDs and BEN are unfit for the purpose.

There is a need, therefore, for improved processes for forming the deposition of uniform nanocrystalline diamond (NCD) films.

SUMMARY

One or more embodiments of the disclosure are directed to a method of forming film. In one or more embodiments, the method comprises: exposing a substrate to a first plasma from a plasma source, the first plasma source comprising one or more of C_xH_y wherein y≥x, carbon dioxide (CO_2), hydrogen (H_2), nitrogen (N_2), and argon (Ar) to provide a treated substrate; incubating the treated substrate with a gas stream and a second plasma to nucleate diamond particles on a top surface of the substrate, the gas stream comprising a hydrocarbon; and exposing the diamond particles to a third plasma having a power greater than 50 W to form a nanocrystalline diamond film on the top surface of the substrate.

Other embodiments of the disclosure are directed to a method of forming a diamond film. In one or more embodiments, the method comprises: exposing a treated substrate to a gas stream to nucleate diamond particles on a top surface of the treated substrate, the gas stream comprising a hydrocarbon; and exposing the diamond particles to a plasma having a power greater than 50 W to form a nanocrystalline diamond film on the top surface of the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

So that the manner in which the above recited features of the present disclosure can be understood in detail, a more particular description of the disclosure, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this disclosure and are therefore not to be considered limiting of its scope, for the disclosure may admit to other equally effective embodiments. The embodiments as described herein are illustrated by way of example and not limitation in the figures of the accompanying drawings in which like references indicate similar elements.

FIG. **1** illustrates a process flow diagram of a method for depositing a nanocrystalline diamond film according to one or more embodiments;

FIG. **2**A illustrates a schematic cross-sectional view of a substrate during the method according to one or more embodiments;

FIG. **2**B illustrates a schematic cross-sectional view of a substrate during the method according to one or more embodiments;

FIG. **2**C illustrates a schematic cross-sectional view of a substrate during the method according to one or more embodiments;

FIG. **2**D illustrates a schematic cross-sectional view of a substrate during the method according to one or more embodiments; and

FIG. **2**E illustrates a schematic cross-sectional view of a substrate during the method according to one or more embodiments.

DETAILED DESCRIPTION

Before describing several exemplary embodiments of the disclosure, it is to be understood that the disclosure is not limited to the details of construction or process steps set forth in the following description. The disclosure is capable of other embodiments and of being practiced or being carried out in various ways.

As used in this specification and the appended claims, the terms "precursor," "reactant," "reactive gas" and the like are used interchangeably to refer to any gaseous species that can react with the substrate surface.

A "substrate" as used herein, refers to any substrate or material surface formed on a substrate upon which film

processing is performed during a fabrication process. For example, a substrate surface on which processing can be performed include materials such as silicon, silicon oxide, strained silicon, silicon on insulator (SOI), carbon doped silicon oxides, amorphous silicon, doped silicon, germanium, gallium arsenide, glass, sapphire, and any other materials such as metals, metal nitrides, metal alloys, and other conductive materials, depending on the application. Substrates include, without limitation, semiconductor wafers. Substrates may be exposed to a pretreatment process to polish, etch, reduce, oxidize, hydroxylate, anneal and/or bake the substrate surface. In addition to film processing directly on the surface of the substrate itself, in the present disclosure, any of the film processing steps disclosed may also be performed on an under-layer formed on the substrate as disclosed in more detail below, and the term "substrate surface" is intended to include such under-layer as the context indicates. Thus, for example, where a film/layer or partial film/layer has been deposited onto a substrate surface, the exposed surface of the newly deposited film/layer becomes the substrate surface.

As used herein, the phrase "nanocrystalline diamond" refers a solid film of diamond typically grown on a substrate, such as silicon. In one or more embodiments, nanocrystallinity is the result of the enhanced re-nucleation reaction in diamond growth, where the growth of diamond crystal is disrupted due to the fluctuation of surrounding environments such as the amounts of radical species, temperature, and pressure. In one or more embodiments, nanocrystalline diamond layers are mainly comprised of small diamond crystals in nanospheres, or a nanocolumnar shape, and amorphous carbon distributed usually distributed in the positions between surrounding crystals or accumulate in the grain boundaries. Nanocrystalline diamond is used as a hard mask material in semiconductor applications because of its chemical inertness, optical transparency, and good mechanical properties.

One or more embodiments of the disclosure advantageously provide a novel method for the in situ nucleation and growth of nanocrystalline diamond films. Embodiments describe the development and utilization of plasma and gas chemistry for substrate treatment and the nucleation and growth of nanocrystalline diamond films. In one or more embodiments, prior solution-based substrate treatment/cleaning nor additional seeding methods such as sonication with nanodiamonds or mechanical scratching are not required. Likewise, no unique chemicals are required during the process.

In one or more embodiments, a nanocrystalline diamond layer is formed on a substrate. The process of one or more embodiments advantageously produces a nanocrystalline diamond layer with high density, high hardness, high etch selectivity, low stress, and excellent thermal conductivity.

Hard masks are used as etch stop layers in semiconductor processing. Ashable hard masks have a chemical composition that allows them to be removed by a technique referred to as ashing once they have served their purpose. An ashable hard mask is generally composed of carbon and hydrogen with trace amounts of one or more dopants (e.g., nitrogen, fluorine, boron, silicon). In a typical application, after etching, the hard mask has served its purpose and is removed from the underlying layer. This is generally accomplished, at least in part, by ashing, also referred to as "plasma ashing" or "dry stripping." Substrates with hard masks to be ashed, generally partially fabricated semiconductor wafers, are placed into a chamber under vacuum, and oxygen is introduced and subjected to radio frequency power, which creates oxygen radicals (plasma). The radicals react with the hard mask to oxidize it to water, carbon monoxide, and carbon dioxide. In some instances, complete removal of the hard mask may be accomplished by following the ashing with additional wet or dry etching processes, for example when the ashable hard mask leaves behind any residue that cannot be removed by ashing alone.

Hard mask layers are often used in narrow and/or deep contact etch applications, where photoresist may not be thick enough to mask the underlying layer. This is especially applicable as the critical dimension shrinks.

V-NAND, or 3D-NAND, structures are used in flash memory applications. V-NAND devices are vertically stacked NAND structures with a large number of cells arranged in blocks. As used herein, the term "3D-NAND" refers to a type of electronic (solid-state) non-volatile computer storage memory in which the memory cells are stacked in multiple layers. 3D-NAND memory generally includes a plurality of memory cells that include floating-gate transistors. Traditionally, 3D-NAND memory cells include a plurality of NAND memory structures arranged in three dimensions around a bit line.

An important step in 3D-NAND technology is slit etch. As the number of tiers increases in each technology node, to control the slit etch profile, the thickness of the hard mask film has to proportionally increase to withstand high aspect etch profiles. Currently, amorphous carbon (aC:H) films are used due to high hardness and easy to strip after slit etch. However, amorphous carbon hard mask films have delamination at bevel and poor morphology, leading to pillar striations.

One or more embodiments of the disclosure are described with reference to the Figures. FIG. **1** illustrates a process flow diagram of a method **100** according to one or more embodiments. FIGS. **2**A through **2**E illustrate schematic cross-sectional view of a substrate **102** being processed according to the method of one or more embodiments.

Referring to FIGS. **1** and **2**A-**2**B, a method **10** of forming a nanocrystalline diamond film **120** is described. In some embodiments, the method **10** comprises, at operation **12**, treating a substrate **102** with a plasma **101** from a plasma source **112** to form a treated substrate surface **104**. The substrate **102** surface is exposed to a mild first plasma **101** in the first plasma process chamber **100** for a first plasma time period T_{P1} to form treated or pre-treated substrate surface **104**.

As used herein, a "substrate surface" refers to any substrate surface upon which a layer may be formed. The substrate surface may have one or more features formed therein, one or more layers formed thereon, and combinations thereof. The substrate (or substrate surface) may be pretreated prior to the deposition of the molybdenum-containing layer, for example, by polishing, etching, reduction, oxidation, halogenation, hydroxylation, annealing, baking, or the like.

The substrate may be any substrate capable of having material deposited thereon, such as a silicon substrate, a III-V compound substrate, a silicon germanium (SiGe) substrate, an epi-substrate, a silicon-on-insulator (SOI) substrate, a display substrate such as a liquid crystal display (LCD), a plasma display, an electro luminescence (EL) lamp display, a solar array, solar panel, a light emitting diode (LED) substrate, a semiconductor wafer, or the like. In some embodiments, one or more additional layers may be disposed on the substrate such that the polymerizable seed layer may be at least partially formed thereon. For example, in some embodiments, a layer comprising a metal, a nitride, an

oxide, or the like, or combinations thereof may be disposed on the substrate and may have the polymerizable seed layer formed upon such layer or layers. In one or more embodiments, the substrate comprises silicon (Si) or poly-silicon (p-Si). In some embodiments, the substrate comprises a poly-Silicon substrate. In some embodiments, the substrate is chemically and/or physically unmodified.

The first plasma process chamber **100** can be any suitable plasma chamber with any suitable plasma source, such as, but not limited to, remote, microwave, capacitively coupled plasma (CCP), or inductively coupled plasma (ICP). In some embodiments, flow rates and other processing parameters described below are for a 300 mm substrate. It should be understood these parameters can be adjusted based on the size of the substrate processed and the type of chamber used without diverging from the embodiments disclosed herein. In specific embodiments, the mild first plasma **101** comprises one or more of a capacitively coupled plasma, inductively coupled plasma, pulsed discharge plasma, microwave plasma, hot filament, or electron cyclotron resonance plasma.

In some embodiments, the first plasma **101** comprises one or more of an organic species having the empirical formula C_xH_y where y≥x, argon (Ar), molecular nitrogen (N_2), carbon dioxide (CO_2), or molecular hydrogen gas (H_2).

In some embodiments, the first plasma **101** is generated with a power greater than 50 watts, 100 watts, or 150 watts. In one or more embodiments, the plasma treatment may occur at any suitable power. In one or more embodiments, the power is greater than 50 W. In other embodiments, the power is in a range of from 50 W to 12 kW, or in a range of from 51 W to 12 kW, or in a range of from 100 W to 10 kW, or in a range of from 100 W to 5 kW, or in a range of from 100 W to 1 kW.

In some embodiments, the substrate **102** is maintained at a temperature in the range of from 20° C. to 600° C. during formation of the treated substrate surface **104**.

In some embodiments, forming the treated substrate surface **104** comprises more than one cycle of exposure to the mild first plasma **101**. In some embodiments, forming the treated substrate face 104 comprises in the range of 1 to 1000 cycles of exposures to the mild first plasma **101**.

The first plasma process chamber **100** of some embodiments comprises a first plasma source **112**, which may include one or more of a showerhead, electrodes, resonators, linear antenna, and the like. In one or more embodiments, the first plasma source **112** is positioned at a first distance D_1 from the top surface of the substrate **102**. In some embodiments, the first distance, D_1, is greater than or equal to 10 mm, 15 mm, 20 mm, or 25 mm.

Referring to FIG. **1** and FIG. **2**C, at operation **14**, the treated substrate **104** is incubated with a carbon-rich gas stream **108** and a second plasma **106** to nucleate diamond particles forming a diamond nuclei layer **110** on the top surface of the substrate **102**.

In one or more embodiments, the diamond nuclei layer **110** is formed in a second plasma process chamber **150** with a second mild plasma **106** generated by a plasma source **114**. In other embodiments, the diamond nuclei layer **110** is formed in the first plasma process chamber **100** with a second mild plasma **106** generate by a plasma source **114**. In some embodiments, the second mild plasma **106** can be generate by the first plasma source **112** but using different gases (compositions).

The second plasma process chamber **150** and the first process chamber **100** can be any suitable plasma chamber with any suitable plasma source, such as, but not limited to, remote, microwave, capacitively coupled plasma (CCP), or inductively coupled plasma (ICP). In some embodiments, flow rates and other processing parameters described below are for a 300 mm substrate. It should be understood these parameters can be adjusted based on the size of the substrate processed and the type of chamber used without diverging from the embodiments disclosed herein. In specific embodiments, the mild second plasma **106** comprises one or more of a capacitively coupled plasma, inductively coupled plasma, pulsed discharge plasma, microwave plasma, hot filament, or electron cyclotron resonance plasma.

In some embodiments, the gas stream **108** and second mild plasma **106** comprises a hydrocarbon. In one or more embodiments, the hydrocarbon has a general formula of C_mH_n, where m is in a range from 1 to 120, and n is in a range of from 2 to 242. In specific embodiments, the hydrocarbon is selected from one or more of methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), ethene (C_2H_4), propene (C_3H_6), butene (C_4H_8), pentene (C_5H_{10}), hexene (C_6H_{12}), heptane (C_7H_{14}), ethyne (C_2H_2), propyne (C_3H_4), butyne (C_4H_6), pentyne (C_5H_8), hexyne (C_6H_{10}), and heptyne (C_7H_{12}).

In one or more embodiments, the second mild plasma **106** may include, in addition to the hydrocarbon, one or more of argon (Ar), molecular nitrogen (N_2), carbon dioxide (CO_2), or molecular hydrogen gas (H_2). In one or more embodiments, the gas stream **108** comprising the hydrocarbon is co-flowed with one or more of argon (Ar), molecular nitrogen (N_2), carbon dioxide (CO_2), or molecular hydrogen gas (H_2) during plasma generation.

In one or more embodiments, the gas stream **108** and the second mild plasma **106** comprise from 5% to 90% hydrocarbon.

In some embodiments, the second mild plasma **106** is generated with a power less than or equal to 15 kilowatts (kW), 12 kW, 10 kW, 9 kW, 8 kW, 7 kW, 6 kW, 5 kW, or 4 kW. In some embodiments, the gas stream **108** is ignited at a power of less than 12 kW to form the second mild plasma **106**. In some embodiments, the second mild plasma **106** is a pulsed plasma with a duty cycle less than or equal to 75%, 70%, 65%, 60%, 55%, 50%, 45% or 40% at a frequency in the range of 50 Hz to 100 Hz, or in the range of 60 Hz to 90 Hz, or in the range of 70 Hz to 80 Hz. In some embodiments, the second mild plasma **106** has a power less than or equal to 6 kW with a duty cycle less than or equal to 50% at a frequency in the range of 70 Hz to 80 Hz. In some embodiments, the substrate **102** is maintained at a temperature in the range of 50° C. to 400° C. formation of the diamond nuclei layer **110**.

In some embodiments, the treated substrate **104** is incubated with the gas stream **108** and the second mild plasma **106** for a time period in a range of from 1 second to 14,400 seconds. In some embodiments, the treated substrate **104** is incubated with the gas stream **108** and the second mild plasma **106** for a time period of less than 4 hours, or less than 3 hours, or less than 2 hours, or less than 1 hour.

In some embodiments, the substrate **102** is positioned at a second distance D_2 from the plasma source **114**. In one or more embodiments, the second mild plasma **106** can be generated by the first plasma source **112** but using different gases (compositions). In some embodiments, the substrate **102** is positioned at a second distance D_2 less than or equal to 12 cm, 11 cm, 10 cm, 9 cm, or 8 cm from the second plasma source **114** or from the first plasma source **112**. In some embodiments, the second plasma source **114** or the first plasma source **112** comprises a showerhead which acts

as an electrode. In some embodiments, the second plasma source **114** comprises a weak microwave plasma source.

At operation **16**, a full nanocrystalline diamond film **118** is grown from the diamond nuclei layer **110**. As used in this manner, the term "grown" means that the full nanocrystalline diamond film **118** is formed on the diamond nuclei layer **110** and may incorporate the diamond nuclei layer **110** into the full nanocrystalline diamond film **118**. The full nanocrystalline diamond film **118** can be epitaxially grown or deposited by any suitable technique known to the skilled artisan.

In some embodiments, growing the full nanocrystalline diamond film **118** occurs in the second plasma process chamber **150** using a strong plasma **120**. In other embodiments, growing the full nanocrystalline diamond film **118** occurs in the first plasma process chamber **100** using a strong plasma **120**. Thus, in one or more embodiments, the first plasma process chamber **100** and the second plasma process chamber **150** are the same chamber. In some embodiments, the full nanocrystalline diamond film **118** is grown using a strong conductively or inductively coupled plasma, microwave plasma, pulsed discharge plasma, microwave plasma, hot filament, or electron cyclotron resonance plasma. In some embodiments, the full nanocrystalline diamond film **118** is grown using a strong microwave plasma.

In some embodiments, the strong plasma **120** comprises a microwave plasma having a power greater than or equal to 3 kW, 4 kW or 5 kW with a duty cycle greater than or equal to 60%, 65%, 70%, 75% or 80%.

In some embodiments, the substrate **102** is maintained at a temperature in the range of room temperature (25° C.) to 750° C. during exposure to the strong microwave plasma **120**. In some embodiments, the substrate **102** is maintained at a temperature greater than room temperature (25° C.), 50° C., 75° C., 100° C., 150° C., 200° C., or 250° C. during exposure to the strong microwave plasma **120**.

During operation **16**, the substrate **102** is positioned a distance D_3 from the third plasma source **130**. In other embodiments, the strong plasma **120** can be generated by the first plasma source **112** and/or the second plasma source **114** but using different gases (compositions) or by a different third plasma source **130**. In some embodiments, the distance D_3 is the same as the distance D_2. In some embodiments, the third distance D_3 is less than the second distance D_2. In some embodiments, the substrate **102** is positioned at a distance from the strong microwave plasma source **130**, or from the first plasma source **112** or from the second plasma source **114**, of less than 12 cm, 11 cm, 10 cm, 9 cm, or 8 cm.

With reference to FIG. **2**E, in one or more embodiments, after being subjected to an extended period of main growth, the high nucleation density on the plasma-treated substrate **102** led to the formation of a fully coalesced nanocrystalline diamond film **120**. In one or more embodiments, FIG. **2**E illustrates how the fully coalesced nanocrystalline diamond film **120** looks after the entire process is completed. The difference between nanocrystalline diamond film **118** and fully coalesced nanocrystalline diamond film **120** is that in the nanocrystalline diamond film **118**, the diamond nuclei from diamond nuclei layer **110** grow in size to become individual, larger diamond particles. These larger diamond particles are, however, isolated from each other. As these large diamond particles continue to grow in size, they eventually come into contact with the neighboring particles and begin to merge/coalesce with each other. This forms a dense, packed nanocrystalline diamond film, which becomes the full coalesced nanocrystalline diamond film **120**.

The disclosure is now described with reference to the following examples. Before describing several exemplary embodiments of the disclosure, it is to be understood that the disclosure is not limited to the details of construction or process steps set forth in the following description. The disclosure is capable of other embodiments and of being practiced or being carried out in various ways.

EXAMPLES

Example 1: Comparative

An untreated wafer was subjected to an incubation process for the in-situ nucleation of diamond particles. During incubation, a carbon-rich gas mixture comprising of 5-90% of methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_6H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), ethene (C_2H_4), propene (C_3H_6), butene (C_4H_{18}), pentene (C_6H_{10}), hexene (C_6H_{12}), heptane (C_7H_{14}), ethyne (C_2H_2), propyne (C_3H_4), butyne (C_4H_6), pentyne (C_6H_8), hexyne (C_6H_{10}) and/or heptyne (C_7H_{12}) was supplied to ensure sufficient carbon source for the nucleation of diamond particles. This was conducted under a relatively weak plasma power of less than 12 kW, 100% duty cycle and 75 Hz, for less than 4 hours. Stage temperature was below 450° C., and the gap was maintained between 2 to 10 cm.

Thereafter, a stronger plasma greater than 50 W and 50% duty cycle was applied for the growth of the diamond particles into nanocrystalline diamond film. This main growth process was conducted at a stage temperature between 100-750° C., and at a gap of less than 10 cm.

Example 2: Carbon-Rich Incubation

A silicon wafer was loaded into a conductively or inductively coupled plasma, microwave plasma, pulsed discharge plasma, hot filament, or electron cyclotron resonance plasma chamber and pre-cleaned/treated with a mild C_xH_y, argon (Ar), molecular nitrogen (N_2), carbon dioxide (CO_2), and/or molecular hydrogen gas (H_2) plasma greater than 50 W to prepare a treated substrate. The stage temperature was maintained between 20-600° C. throughout the entire process and the gap between the stage and plasma source was greater than 20 mm.

The plasma-treated wafer was then subjected to an incubation process for the in-situ nucleation of diamond particles. During incubation, a carbon-rich gas mixture comprising of 5-90% of methane (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_6H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), ethene (C_2H_4), propene (C_3H_6), butene (C_4H_8), pentene (C_6H_{10}), hexene (C_6H_{12}), heptane (C_7H_{14}), ethyne (C_2H_2), propyne (C_3H_4), butyne (C_4H_6), pentyne (C_6H_8), hexyne (C_6H_{10}) and/or heptyne (C_7H_{12}) was supplied to ensure sufficient carbon source for the nucleation of diamond particles. This was conducted under a relatively weak plasma power of less than 12 kW, 100% duty cycle and 75 Hz, for less than 4 hours. Stage temperature was below 450° C., and the gap was maintained between 2 to 10 cm.

Thereafter, a stronger plasma greater than 50 W and 50% duty cycle was applied for the growth of the diamond particles into nanocrystalline diamond film. This main growth process was conducted at a stage temperature between 100-750° C., and at a gap of less than 10 cm.

The nucleation density on untreated (Example 1) and plasma-treated silicon (Example 2) after incubation and a short main growth process was compared. The samples were characterized by scanning electron microscopy (SEM) and

Raman measurement (325 nm laser). It was observed that under identical process conditions, significantly higher nucleation density was achieved on plasma-treated silicon sample (Example 2) as compared to the untreated silicon (Example 1) (4.3 particles μm^{-2}).

After being subjected to an extended period of main growth, the high nucleation density on plasma-treated silicon (Example 2) eventually led to the formation of a fully coalesced monocrystalline diamond film. The morphologies and Raman measurement of a monocrystalline diamond film grown by the in-situ nucleation method are also comparable to that of a ND-seeded wafer prepared by the conventional solution-based seeding. Film properties such as refractive index, extinction coefficient, roughness, hardness and modulus were validated to be comparable to that of the ND-seeded samples. On the other hand, the poor nucleation density on untreated silicon (Example 1) resulted in an incompletely coalesced monocrystalline diamond film with obvious grain boundaries and pinholes throughout the sample.

Spatially relative terms, such as "beneath," "below," "lower," "above," "upper" and the like, may be used herein for ease of description to describe one element or feature's relationship to another element(s) or feature(s) as illustrated in the figures. It will be understood that the spatially relative terms are intended to encompass different orientations of the device in use or operation in addition to the orientation depicted in the figures. For example, if the device in the figures is turned over, elements described as "below," or "beneath" other elements or features would then be oriented "above" the other elements or features. Thus, the exemplary term "below" may encompass both an orientation of above and below. The device may be otherwise oriented (rotated 90 degrees or at other orientations) and the spatially relative descriptors used herein interpreted accordingly.

The use of the terms "a" and "an" and "the" and similar referents in the context of describing the materials and methods discussed herein (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the materials and methods and does not pose a limitation on the scope unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the disclosed materials and methods.

Reference throughout this specification to "one embodiment," "certain embodiments," "one or more embodiments" or "an embodiment" means that a particular feature, structure, material, or characteristic described in connection with the embodiment is included in at least one embodiment of the disclosure. Thus, the appearances of the phrases such as "in one or more embodiments," "in certain embodiments," "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily referring to the same embodiment of the disclosure. In one or more embodiments, the particular features, structures, materials, or characteristics are combined in any suitable manner.

Although the disclosure herein has been described with reference to particular embodiments, it is to be understood that these embodiments are merely illustrative of the principles and applications of the present disclosure. It will be apparent to those skilled in the art that various modifications and variations can be made to the method and apparatus of the present disclosure without departing from the spirit and scope of the disclosure. Thus, it is intended that the present disclosure include modifications and variations that are within the scope of the appended claims and their equivalents.

What is claimed is:

1. A method of forming a nanocrystalline diamond film, the method comprising:

exposing a silicon substrate to a first plasma from a plasma source with a first plasma power in a range of from 50 W to 12 kW, the first plasma source comprising one or more of C_xH_y wherein $y \geq x$, carbon dioxide (CO_2), hydrogen (H_2), nitrogen (N_2), and argon (Ar) to provide a treated substrate;

incubating the treated substrate with a gas stream and a second plasma to nucleate diamond particles on a top surface of the substrate, the gas stream comprising a hydrocarbon and the second plasma having a power less than or equal to 15 kW; and

exposing the diamond particles to a third plasma having a power greater than 50 W to form a nanocrystalline diamond film on the top surface of the substrate, the third plasma comprising a microwave plasma with a duty cycle greater than or equal to 60%.

2. The method of claim **1**, wherein the hydrocarbon has a general formula of C_mH_n, where m is in a range of from 1 to 120, and n is in a range of from 2 to 242.

3. The method of claim **2**, wherein the gas stream further comprises one or more of carbon dioxide (CO_2), hydrogen (H_2), nitrogen (N_2), and argon (Ar).

4. The method of claim **3**, wherein the gas stream comprises from 5% to 90% of the hydrocarbon.

5. The method of claim **1**, wherein the gas stream is ignited at a power of less than 12 kW.

6. The method of claim **1**, wherein the treated substrate is incubated with the gas stream and the second plasma for a time period of less than 4 hours.

7. The method of claim **1**, wherein the treated substrate is maintained at a temperature of less than 450° C. during incubation.

8. The method of claim **1**, wherein the diamond particles are maintained at a temperature in a range of from 100° C. to 750° C. during formation of the nanocrystalline diamond film.

9. The method of claim **1**, wherein incubating the treated substrate is conducted with a duty cycle of less than 100%.

10. The method of claim **1**, wherein the third plasma has a duty cycle greater than 70%.

11. The method of claim **1**, wherein the substrate is exposed to the first plasma at a temperature in a range of from 20° C. to 600° C.

12. The method of claim **1**, wherein the substrate is exposed to the first plasma at a distance of greater than 2 cm.

13. The method of claim **1**, wherein when the treated substrate is incubated with the gas stream, the gas stream is about 2 cm to 10 cm away from the top surface of the treated substrate.

14. The method of claim 1, wherein when the diamond particles are exposed to the third plasma, the third plasma is less than 10 cm away from the top surface of the substrate.

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